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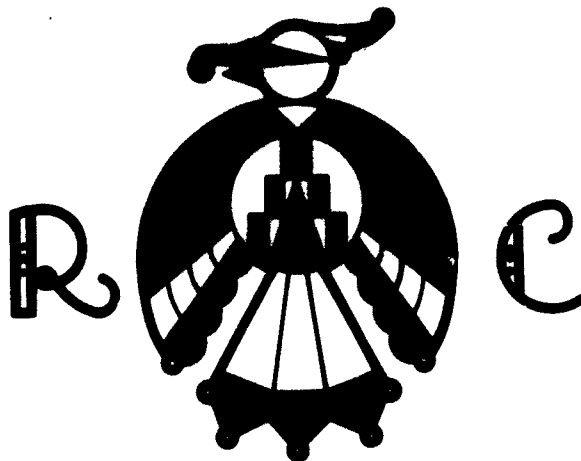
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**THE PREPARATION OF HIGH PURITY RARE EARTH METALS
BY ZONE REFINING**

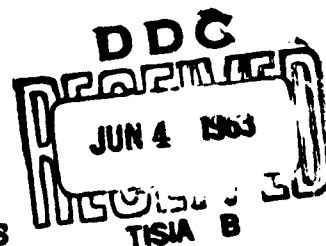
C. J. Heinink

**CONTRACT NO. AF 19(604)-7491
PROJECT 4608
TASK 460802**

FINAL REPORT

**Report Period
January 1, 1962 to January 31, 1963**

**Prepared for:
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS**



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**THE PREPARATION OF HIGH PURITY RARE EARTH METALS
BY ZONE REFINING**

C. J. Heinink

**RESEARCH CHEMICALS
Division of Nuclear Corporation of America
Phoenix, Arizona**

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FINAL REPORT

**THE PREPARATION OF HIGH PURITY RARE EARTH METALS
BY ZONE REFINING**

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ABSTRACT

Ultra high purity rare earth metals, Samarium, Europium, Gadolinium with total impurities of less than .1 ppm were attempted to be made. Methods of separation, reduction and purification were: ion exchange, dry fluoride preparation, metallothermic reduction, vacuum distillation, zone refining by induction heat and electron beam melting. Gas chromatography was investigated as an analytical tool for determination of oxygen in metals.

PURIFICATION OF RARE EARTH OXIDES BY ION EXCHANGE

Several hundred grams of gadolinium, samarium and europium have been processed through the ion-exchange columns to 99.999% purity, and were processed into fluorides. Previously, conversions of oxides to fluorides were accomplished with ammonium bifluoride. In the present series, a direct reaction with anhydrous hydrogen fluoride was employed. Oxides were placed in platinum boats and the reaction was carried out in a tube furnace at 800°C.

For purification of the oxides, the same techniques reported in Scientific Report No. 2 "The Preparation of High Purity Rare Earth Metals," April, 1962, were applied on the ion exchange process except for some minor changes. For instance, during the first column run in which 75% of the Rare Earth is purified to one order of magnitude, the following change was made:

Through a better understanding of the elution behavior and segregation coefficient of one Rare Earth with respect to another, we were able to predict the segregation coefficients of most of the impurities in the first five and last three to four cuts. Whereas for a

100 gm charge about 20 cuts have been taken in the past, now only one large center cut is necessary, which produces 99.99% of the Rare Earth. On the second column about 20 cuts are necessary, since at those low impurities the theory of the elution behavior does not apply as well and only 20% of the original charge from column #1 is 99.999% pure.

PURIFICATION OF EUROPIUM BY ION EXCHANGE

Europium having a di- and tri-valent state is usually purified by the Mercury Cathode Method. (See Scientific Report #2, April, 1962.)

As a final purification step Europium having a stability constant of 17.4 with EDTA can easily be purified by ion exchange resulting in a 99.999 or better percent purity. The method was exactly the same as used for Praeseodymium, Gadolinium and Lutetium. (See Scientific Report #2, April, 1962.)

PREPARATION OF GADOLINIUM METAL

Equipment:

The furnace used for the Gadolinium metal reductions was built by Consolidated Vacuum Corporation. It was

Consolidated's type FIM-50 Vacuum Induction Melting Furnace.

The pumping system of the FIM-50 furnace produces the low pressures required for a gas-free atmosphere, while providing ample capacity up to a pressure of 1.5 mm Hg for handling the surges caused by dioxidation and pouring. This unit is supplied complete with necessary pumps, valves, gauges, and piping. All vacuum line valves are pneumatically operated. Controls for the pumps and valves are mounted in a cabinet next to the stationary section of the furnace. A CVC Pirani gauge, also mounted in the cabinet, indicates the pressures in chamber and forepump on two direct-reading scales from 1 to 2000 microns Hg. A filter is provided between the gauge tube and the furnace to protect the tube's sensing elements from contamination by metallurgical duct.

The standard pumping system consists of a CVC KS-600 diffusion-ejector pump, a 130 cfm mechanical pump for both roughing and backing, and a 3.5 cfm mechanical holding pump.

Approximately one minute is required to rough a clean, dry and empty system down to 750 microns of mercury. An additional two minutes are necessary to further reduce the pressure to three microns of mercury. In-

leakage is less than 156 micron-cubic feet per hour as measured on a McLeod gauge.

The specifications of the furnace are:

1. Power requirements:

(a) KS600 pump 3.7 Kilo-watts, 200 volts, single phase

(b) 130 cfm Mechanical Pump 220/440 Volts, three phase

(c) 3.5 cfm Mechanical Pump 110/220 Volts, single phase

2. Air: 60 - 80 pounds per square inch

3. Water:

(a) Pressure 40 pounds per square inch

(b) Furnace Shell 5 gallons per minute

(c) KS600 pump .3 gallons per minute

(d) 130 cfm pump 1.5 gallons per minute

4. Dimensions (including pumping system):

(a) Height 7 feet

(b) Length 10 feet, 4 inches

(c) Width 3 feet, 6 inches

Procedure

Fifty grams of high purity gadolinium fluoride were placed into a 1-1/2 x 2-1/2 inch tantalum crucible. Fifteen grams of distilled calcium were added on top of the charge. (Gd to Ca ratio equals .2806 to 1 plus a 3% excess.) The crucible was inserted in a graphite susceptor. The susceptor was then placed in the CVC furnace. The furnace was evacuated to one micron and backfilled with gettered argon to fifteen inches. The backfilling was repeated four times. The charge was heated to 1377°C (melting point of gadolinium fluoride). At this temperature the reduction took place. The charge was allowed to cool and the slag was removed. After the slag was removed the charge was put back into the furnace for a cleaning process. This process consists of heating the metal until it is molten, under a high vacuum (one micron). The higher vapor pressure metals distill off and in this way the gadolinium is cleaned. The charge was then removed and a hole was drilled in the bottom of the tantalum crucible. A small mold was inserted beneath the tantalum crucible. The gadolinium was cast by heating it to a molten stage, allowing the metal to flow into the mold. Care should be taken so that there is a space between the mold and the bottom of the crucible. In some of the early experiments the casting was not complete because of the apparent pressure build-up in the mold. This was corrected by allowing

a small space between the mold and the crucible. (See Figure #1)

ZONE REFINING

Whenever purification is possible by crystallization (2) from the melt, zone melting can be applied. Zone melting may therefore be used to purify compounds and also elements. The usefulness of zone refining procedures lies not only in the wide range of materials which can be purified, but also in the ease of operation. Apparatus can be extremely simple and easily made in the laboratory and yet a remarkable high purity can be obtained. Naturally for the best results a more complicated apparatus may be required.

Zone melting was accomplished by Bridgman in 1926. He showed that when a molten zone was passed along an ingot, the impurities were segregated by the molten zone. By this technique he was able to purify the material. Complete solidification of the ingot results in a distribution of impurities along its length. By selecting the parts of the ingots which had solidified first, the process could be repeated and considerable purification obtained. This method of solidification has been termed normal freezing.

The major advance, however, came in 1952 when Pfann (3) observed that if only a small section of the ingot was molten at any time the molten zone could be passed re-

peatedly through the ingot sweeping impurities with each pass. Subsequently he and others developed the theory and practice of zone melting, as it came to be known, so that it now represents one of the most useful methods available for the purification of a wide variety of materials.

DISTRIBUTION CO-EFFICIENT AND EQUILIBRIUM DIAGRAM

Not all impurities are swept along in the zone and not all move along to the same extent. A factor K - the segregation coefficient - is used as a measure of the efficiency of the process. This factor was defined by Pfann, as the ratio of the concentration of impurity in the solid, to that in the liquid, which is in equilibrium with it. The result of zone melting can be predicated, if the appropriate equilibrium diagram is available. In the case of the rare earth metals there is very little information available which makes any preliminary predictions very difficult. (4)

The definition follows from the fact that the chemical potential μ of the impurity may be expressed by

$$\mu = \mu_0 = RT \log a$$

Where μ is a constant, T the absolute temperature and a is the activity of the impurity. The chemical potential of the impurity in phase 1 is

$$\mu_1 = \mu_{01} + RT \log a_1$$

and in phase 2 it is

$$\mu_2 = \mu_{O2} + RT \log a_2$$

At equilibrium $\mu_1 = \mu_2$ and hence $a_1 = a$ constant.

In dilute solution $a_1 / a_2 = C_1 / C_2$ where C_1 and C_2 represents the concentration of impurity in phase 1 and phase 2.

Solid/melt equilibrium diagrams have been obtained experimentally for a great many metallurgical systems and the distribution coefficient can be usefully thought of in terms of these "phase" or "equilibrium" diagrams.

The distribution of impurities along an ingot after zone melting, or concentration profile, depends primarily on the segregation coefficient K . Equations describing the concentration profile have been derived by a number of authors and these can be solved if certain simplifying assumptions are made.

Pfann derived an equation for the concentration profile after normal freezing in the following way. He assumed that the system was a 2 phase one a homogeneous melt, that the diffusion of impurity in the solid was negligible, and that K was constant. Such assumptions cannot always be substantiated in practice, but they are useful simplifications, if g is the fraction of the original volume which had frozen and s the amount of solute remaining in the liquid.

So the total amount of solute, C the solute concentration in the solid at the liquid/solid interface (in units of solute per unit volume of solid). \underline{C} the solute concentration in the liquid and \underline{K} the distribution coefficient, then

$$1. \quad C = K C_1 \text{ (by definition)}$$

and

$$2. \quad C_1 = \frac{s}{1-g} \quad C = \frac{ks}{1-g}$$

If a further fraction, dg , of the ingot, is allowed to solidify, then concentration C in this solidified portion is

$$C = - \frac{ds}{dg}$$

From equations 1 and 2, and integrating

$$\text{and} \quad \int_{s_0}^s \frac{ds}{s} = \int_0^g \frac{-k}{1-g} dg, \quad s = s_0 (1-g)^k$$

$$C = - \frac{ds}{dg} = k s_0 (1-g)^{k-1}$$

Since the original volume was taken as unity, $s_0 = C_0$, where C_0 is the original solute concentration. Hence the concentration along the ingot is given by

$$C = K C_0 (1-g)^{k-1}$$

If the values C and C_0 are known for a particular ingot, K can be calculated.

Vapor Phase

Van den Boomgaard first considered the zone melting of a material containing a volatile impurity. The composition of the melt (and hence the solid) at any time is determined

by the rate of reaction of vapor with the liquid as well as by the deposition and solution of solid which occurs as the zone moves along. (5) If the rate of reaction is very rapid, equilibrium between vapor and liquid is reached at once, and if a constant vapor pressure is maintained the composition of the melt (and hence of the solid) will be uniform. Van den Boomgaard's observations are important, not only in that they show how the composition of the ingot can be controlled by an impressed vapor pressure, but also because they emphasize that the impurity can be transferred along the ingot in the vapor phase. If, for instance, a gadolinium ingot contains small amounts of europium, which has a high vapor pressure, the transfer of this impurity along the ingot can take place via the vapor phase. The europium would evaporate from the liquid zone and condense on the cooler parts of the gadolinium ingot where it would be remelted by subsequent zones.

ZONE REFINING BY INDUCTION HEATING

Several attempts to zone refine Rare Earth were made using induction heat in a low argon pressure. A 2.5 KW Lepel Generator was used as a power source. Experiments were conducted using different coil designs to narrow the molten zone.

A single turn coil did not give sufficient heat to melt any Rare Earth samples. The best design was found to be a flat pancake coil having 3 to 4 turns attached to a 1/32" split annulus baseplate. A modification of this design was finally used and the copper tubing of the coil was flattened to 1/8". It was found that no baseplate was necessary on this type of coil. Several 6" rods of gadolinium metal (99% purity) 1/4" in diameter were used for these experiments. The final purity of the metal has not been checked since the purpose of the tests was to determine the zone width of the coil and to determine how closely we could control the power input and temperature. The plate current was recorded on a strip chart recorder and very fine control was obtained. By further investigation of the samples we found a definite large crystal formation. Crystals as large as 1/4" were present in the middle portion of the rod. (See picture #2.)

ELECTRON-BEAM ZONE REFINING

Electron-beam zone refining has considerable advantages over zone refining by induction heating, principally the close control of both the zone width and the beam power that is possible. The high vacuum that is essential to the technique is an advantage in that additional refining is obtained

by pumping off volatile constituents from the melt, but appears to limit the technique to the lower vapor pressure metals.

An electron-beam refining apparatus has been constructed. The vacuum system consists of a 14" bell jar pumped by a 4" diffusion pump. Rotary motion to drive the sample traverse is provided through a rotary feed-through with double "O"-ring seals that are provided with pump-down port between the sealing points. The system is quite tight, and vacuums in the 10^{-5} to 10^{-6} minimum range are easily obtained even without a cold trap.

Beam power is obtained from a 0-5 KW, 0.5 Ampere supply. The electron source is a 1-inch diameter ring of .010" tungsten wire that is heated by a 30 Ampere supply. Deflection plates are located .25" above and below the filament. A negative bias of about 300 volts is adequate to cut off the beam, and very narrow zones can be obtained by controlling the bias voltage on the deflection plates. Since the beam current is an extremely critical function of the bias current when the beam is close to the cut-off point, the bias voltage is supplied by an electronically regulated supply. (See Figure 4.)

Actual control of the temperature of the molten zone presents many problems which, while probably not insoluble, would have required for their solution considerable time. It was decided, therefore, to devise a feedback control system that would maintain constant power into the beam. A Beckman Hall Multiplier element is supplied with signals proportional to the accelerating voltage and to the beam current. The output signal, which is proportional to the instantaneous beam power, is then compared with a precise reference voltage. The error signal is amplified by a chopper-stabilized amplifier that drives a magnetic amplifier. The output of the magnetic amplifier then controls the filament current.

The control system appears to work very well, and can maintain the power constant with a 2 to 1 variation of accelerating voltage. Once the control point is set, the diameter of the zone refined rod stays remarkably constant.

A rod of relatively impure gadolinium was selected for the first run in the apparatus. The spectrographic analysis of various sections of the rod after 2 passes at approximately 1" per hour is included below. Sample 1 is from the starting material, Sample 2 is from top of the zone-refined section and Sample 3 is from the center of the zone-refined section.

	<u>Gd</u>	<u>Sm</u>	<u>Tb</u>	<u>Dy</u>	<u>Y</u>	<u>Eu</u>	<u>Fe</u>	<u>Si</u>	<u>Mg</u>	<u>Ca</u>
1.	VS	.2	.1	.03	.03	.03	.3	T	.01	.01
2.	VS	.1	.1	---	.03	.05	.4	.01	.01	.005
3.	VS	.05	.1	---	.01	---	.1	T	.005	.005

It can be seen that the material was substantially upgraded. Sm and Dy were undoubtedly removed by evaporation. All of the other impurities, with the exception of terbium, appear to be segregated in the top of the refined zone. It should be noted that determination of segregation coefficients for the Rare Earths with respect to one another and to their more common impurities would be a very worthwhile undertaking.

Samples of holmium and samarium have been tried out in the system, and indicate that considerable difficulty will be experienced with metals having high vapor pressures.

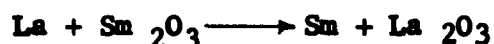
Breakdown in the metal vapor occurred at very low accelerating voltages. See table (3) vapor pressures. Additional rods of higher purity gadolinium were prepared for running in the electron-beam apparatus, which were 1 inch long and 3/8 inch in diameter. Each ingot was welded in the electron beam furnace to two rods of gadolinium metal, one on each end, having a purity of 99.9%.

After the welding was completed the furnace temperature was brought up slowly, allowing the gadolinium to out-gas.

(See figure 5) Care was taken to keep the temperature well below the melting point of the metal in the first part of the operation. When out-gassing occurs and the vacuum decreases to 10^{-3} , the temperature goes up. Care should be taken to control the temperatures closely to avoid melting the rod in halves. After the out-gassing step a molten zone of .125 inch was then formed at the bottom of the ingot which was moved up by mechanical means at a traveling rate of 1 inch per hour. (See figure 6.) The ingot was zone refined 5 times and with the last four runs the vacuum was kept to 10^{-7} . A 2 gm sample was then cut, using the electron-beam, to be analyzed on a mass-spectrograph at the Air Force Cambridge Research Laboratories.

DISTILLATION OF SAMARIUM AND EUROPIUM

Due to the high vapor pressures of Samarium and Europium (see table 3) attempts to zone refine those metals by electron-beam were unsuccessful. The samples then were double distilled as follows, using a ratio of 1:1 plus 10% excess of oxide to Lanthanum, the charge was heated in a tantalum crucible in a high vacuum to effect the reactions:



The tantalum crucible was sealed on top with a tantalum sheet and a copper heat sink placed on top of it. The lower portion of the tantalum crucible was maintained at the highest temperature (1350°-1400°C) so that the volatile metals were recovered in yields greater than 75%, as bright crystalline condensates on the tantalum sheet placed on top of the crucible. Samples of Europium and Samarium were sent to the Air Force Cambridge Research Laboratories for analysis on a mass-spectrograph.

One of the several methods that have been employed in the past for zone refining is the arc image. However, since it approximates a point source, it has been used primarily

for crucible melts, and is not particularly adaptable to floating zones. If a series of point source arcs were imaged radially onto a bar, however, it should be possible to melt a fairly sharp zone. An extension of this notion has led to the design of an apparatus to focus radially the image of a tungsten ring filament onto a 1/4 inch bar.

The apparatus consists essentially of a highly polished, hollow toroidal aluminum mirror that focuses the image of a 2 inch ring of 0.040 tungsten wire on a 1/4 inch ring at the center. Although the geometry of the system is such that, at a superficial glance, a true radial image would seem to be produced. Actually, each point on the wire acts as a source for the entire mirror, although it is truly focused by only one portion of the mirror. Hence a sharp image of the hot filament is not produced; however, probing of the image with a thermocouple has demonstrated a substantial concentration of energy in a fairly narrow zone.

The principle advantage to be anticipated of the system is the ability to melt a narrow zone in a rod held within a quartz tube under inert gas pressure. In order to run the tungsten filament at high temperatures, the entire system must be contained in either a vacuum or in

an inert atmosphere in order to prevent oxidation of the tungsten. The housing for the system has not been completed, so that actual zone-refining runs have not yet been made.

OXYGEN ANALYSES BY MEANS OF ARC SPARK AND GAS CHROMATOGRAPH

Sample size and sample introduction are extremely important in gas chromatography because of their influence upon the apparent retention volume, the shape of the peaks obtained and subsequently upon the ability of a given column to separate the components of the sample. Several authors (6.7) have discussed the theory of gas chromatography, utilizing the plate theory of Martin and Syngé which involves several simplifying assumptions:

1. Samples are charged to the head of the column so that the initial charge is instantaneously contained with the first theoretical plate.
2. No change in the volume of a volume element of mobile phase occurs as it passes through the columns.
3. The partition coefficient for the distributing material is constant throughout the column.
4. All rate effects can be taken account by the concept of theoretical plates.

Two extreme cases are considered, the first case being designated "plug flow" and corresponds to a "plug" of solute gas mixture of constant composition being charged to the head of the column. The other case corresponds to mixing of the mobile phase in a vaporizer in such a manner as to introduce the vapor without dilution to the head of the column initially, but the sample concentration falls off exponentially with time to zero. Mathematically, "plug flow" gives rise to symmetrical peaks while "exponential flow" gives rise to peaks having a definite tail. In practice, the normal technique of sample introduction lies somewhere between the two cases.

Porter et al (9) compared elution curves, which were calculated on the basis of "plug flow" and "exponential flow," with an elution curve obtained by means of their instrument which had a sample introduction system containing a heater vaporizer block at a distance from the column head. The sample was introduced into the heated vaporizer block, vaporized at some indetermined rate and carried to the column head by the mobile phase. The experimental conditions were chosen such that the activity coefficient was nearly unity and thus the partition coefficient was nearly constant throughout the column.

The results of this comparison are shown in figure (8).

It should be noted that the experimental curve closely approaches that calculated for exponential flow. Figures #9 and #10 show the results of plug flow and exponential flow under varying time conditions.

Selection of By-pass and Valve Systems

To deliver gaseous samples into a gas chromatograph it is generally accomplished by means of either a "by-pass" system or a six part gas sample valve. Both of these systems are designed to introduce a known volume of gas sample into the mobile phase. Other authors (10,11) have used similar systems which allow for interchangeable sample volumes and the operation of only a single stop cock necessary to introduce the sample. Most commercial instruments have employed a modification of the six part gas sampling valve. (See figure 7.) The gas sampling valve is generally connected to some type of gas handling system which allows the sample to be introduced into the valve without contamination. The sample size is determined by the volume, pressure and temperature. Referring to the diagram figure 7, the sample is delivered into the sample valve when the valve is in position 1. When the desired sample is contained within the sample volume tube, the valve is moved into position 2. At this point the mobile phase sweeps through the sample

volume introducing the sample into the chromatograph in a condition which approaches "plug flow." The major advantage of this system over the by-pass system is that while it can be connected to a gas handling system and used in the same manner as the by-pass system, it can also be used in a gas stream, where repetitive sampling is desired,

ANALYTICAL APPROACHES FOR DETERMINATION OF IMPURITIES OF LESS THAN 1 PPM

Several different analytical procedures have been investigated concerning the determination of low impurities in the parts per million region.

MASS SPECTROGRAPH

The modern mass spectrograph is a development of the classic work of Aston. Aston showed that atoms and isotopes can be separated by virtue of their detection in electrostatic and magnetic fields. The sample is prepared in the form of two electrodes .003 m² cross section, which are mounted close together in the ion source in a vacuum of about 10⁻⁷ mm Hg. When a high voltage is applied between them a spark occurs and positive ions are produced. These are accelerated in an ion gun and then pass through electrostatic and magnetic fields where they suffer deflections according to their e/m ratio, where e is the electronic

charge and m the mass of the ion. Ions of the same e/m ratio are then focused and recorded as lines on a photographic plate.

In principle, all elements are about equally sensitive to detection, so that a complete analysis can be obtained. The sensitivity of detection may be .01 ppm. The method has the additional advantage over the conventional spectrograph in that the mass spectrum of an element is extremely simple. With some experience, therefore, lines can be recognized easily. For more accurate quantitative analyses, techniques similar to those in use in conventional spectroscopy, can be used. Perhaps the greatest difficulties which have been experienced with mass spectrographs are the mechanical ones of ensuring a sufficiently good vacuum. The construction of the ion source, so that a sample truly representative of the solid is vaporized, and finally the elimination of incidental impurities which give rise to high blank values and anomalous readings. A technique known as isotope dilution may be used to increase the sensitivity of detection of impurities. This principle can be applied to any element which has more than one isotope. It involves addition to the specimen under examination of a sample of the impurity element to be detected which has one isotope artificially enriched.

The element is then extracted chemically and the isotope ratio compared with that of the added material to give the change in isotope ratio. From this the impurity concentration can be calculated. A review of the mass spectrometer in chemical analysis has been given by Waldron.

INFRA-RED SPECTROSCOPY

Prawson and Nielsen report that infra-red absorption spectra have proved of special value in the identification and analysis of organic systems. A source of infra-red radiation which has been split into component wave lengths is passed through a sample of the host material which is usually in the form of a dilute solution. The amount of radiation passing through the sample at this wave length is then measured with a suitable detector, and the percentage absorption is calculated. Repetition for various wave lengths provides a complete infra-red spectrum.

In the Perkin-Elmer and Grubb-Parsons instruments, which are very commonly used, the spectrum from 0.5μ upwards is recorded automatically on a chart up to the longer the wavelength limit, which will depend on the prism material, e.g., 15μ for Na Cl. As mentioned before, this system is used mainly for organic systems, however, a possible use occurs when an organic complexing agent is added to a Rare Earth solution since then a trace of the metal complex may be detected.

RADIOACTIVATION ANALYSES

In the technique the sample to be analyzed is bombarded by sub-atomic particles until a detectable level of activity is induced in the impurity to be analyzed. In favorable cases the matrix material, which is activated at the same time, has a short lifetime so that after a certain time the activity from the sample is principally due to the impurities. Thus the type and amounts of impurities can be ascertained by an analysis of the radioactivity, i.e., the energy, type and rate of decay of emitted particles. If the mixture of impurities is too complex or further confirmation is required, then a chemical separation must be made. The separation of a trace of a particular (radioactive) impurity may be simplified if a quantity of the same (inactive) impurity is added prior to the separation. By weighing the amount of impurity added before separation and the amount after separation, the percentage recovery may be estimated, this being also the percentage recovery of the radioactive trace. The amount of radioactive trace can then be corrected for 100 percent recovery and hence the amount initially present in the sample calculated. Usually a comparative method of estimation is used and in this case the mass of impurity A in the sample

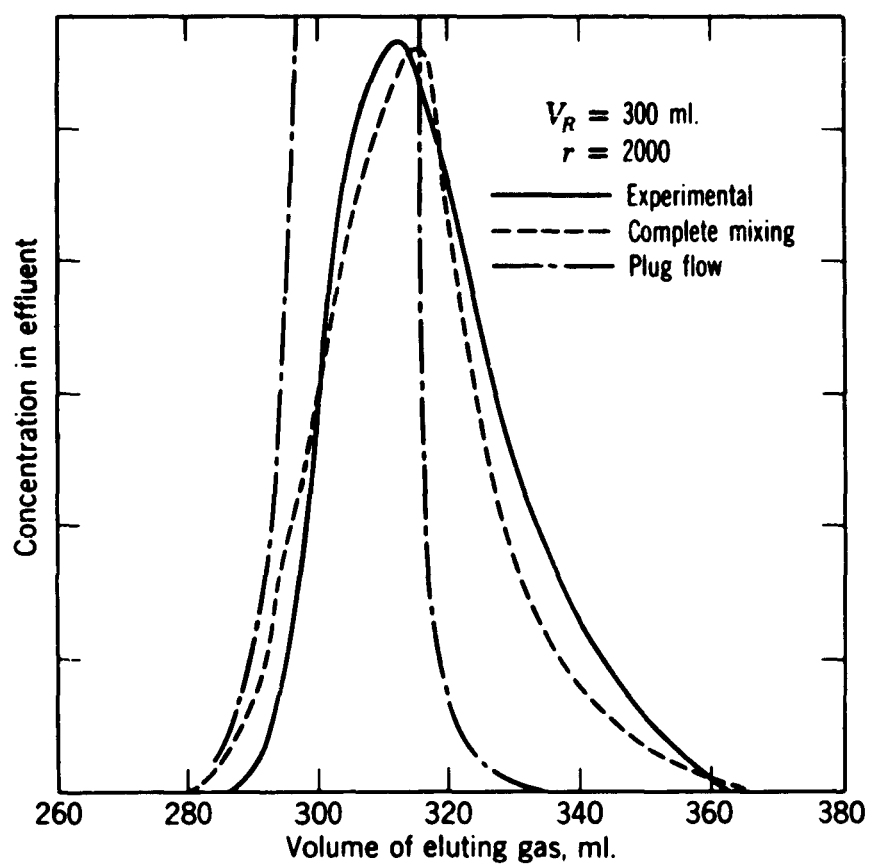
= mass of A in the standard multiplied by

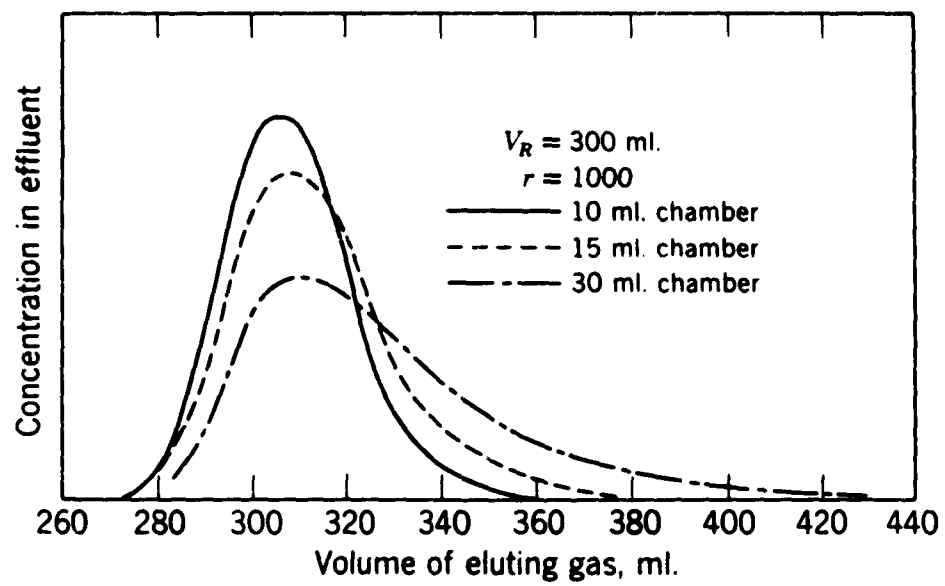
$$\frac{\text{Activity of sample corrected for 100\% recovery}}{\text{Activity of standard corrected for 100\% recovery}}$$

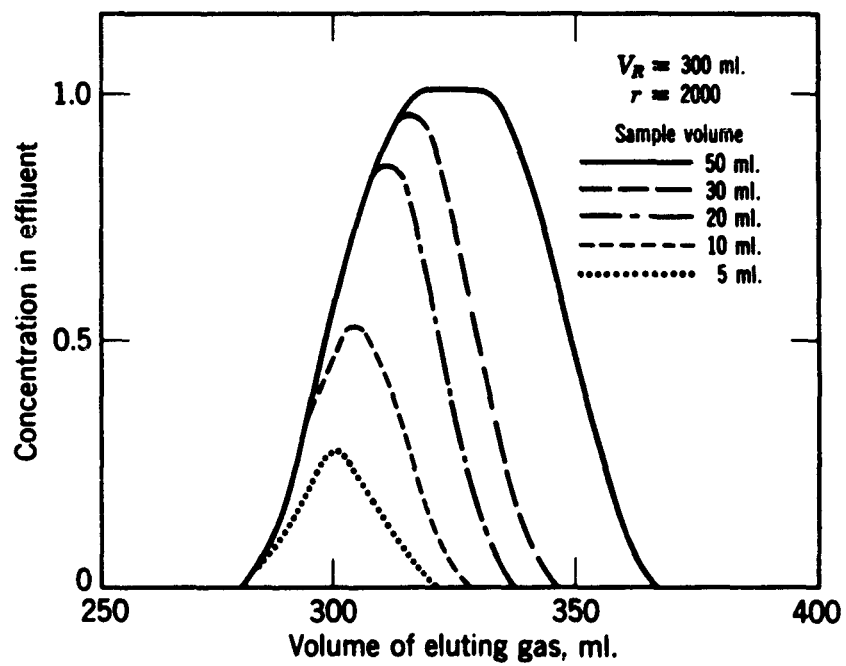
That only one radioactivity impurity has been isolated may be checked both by chemical methods and by the nature and lifetime of the emitted particles. Detection of sub-microgram quantities of impurity (10^{-6} to 10^{-10} gm) is easily possible by this method. The sensitivity limit depending largely on the capture cross section or amount of radioactivity which can be induced in the impurity.

REFERENCES

1. "The preparation of high Purity Rare Earth Metals"
Scientific Report #2 April (1962) C. J. Heinink
2. Preparation of Single Crystal; Lawson and Nielsen
3. Zone Refining; Pfann
4. "Contribution to Mathematics of Zone Melting" Burris, L.
Stockman, C. H., and Dillon, I. G., Trans. AIME 203 p. 1017-1023 (1955)
5. "Mathematical Methods for zone melting processes" Reis, H.,
Trans. AIME 200 p. 1053-1059 (1954)
6. "The theoretical plate concept in column separation"
Glueckauf, E., Trans. Faraday Soc 51 p. 34-44 (1955)
7. "Longitudinal diffusion and resistance to mass transfer as
a cause of non ideality in chromatography" Van Heempter,
J. J., Zuiderweg, F. T., and Klinkenberg, A., Chem. Eng.
Soc. 5 p. 271 (1956)
8. "A theory of chromatography" Martin, A. J. P., and Hynge,
R. L. M., Biochem Journal 35 p. 1358-68 (1941)
9. "The determination of partition coefficients from gas
liquid partition chromatography" Porter, P. E., Deal, C.H.,
and Stross, F.H., Journal A.M. Chem. Soc. 78 p. 2999-3006 (1956)
10. "Applications of vapor-phase-chromatography in the gas an-
alytical field" Van de Craats, F., Anal. Chim. Acta 14
p. 136-39 (1956)
11. "Stopcock for gas chromatography" Glew, D. M., and Young,
D. M., Anal. Chem. 30 p. 1890 (1958)







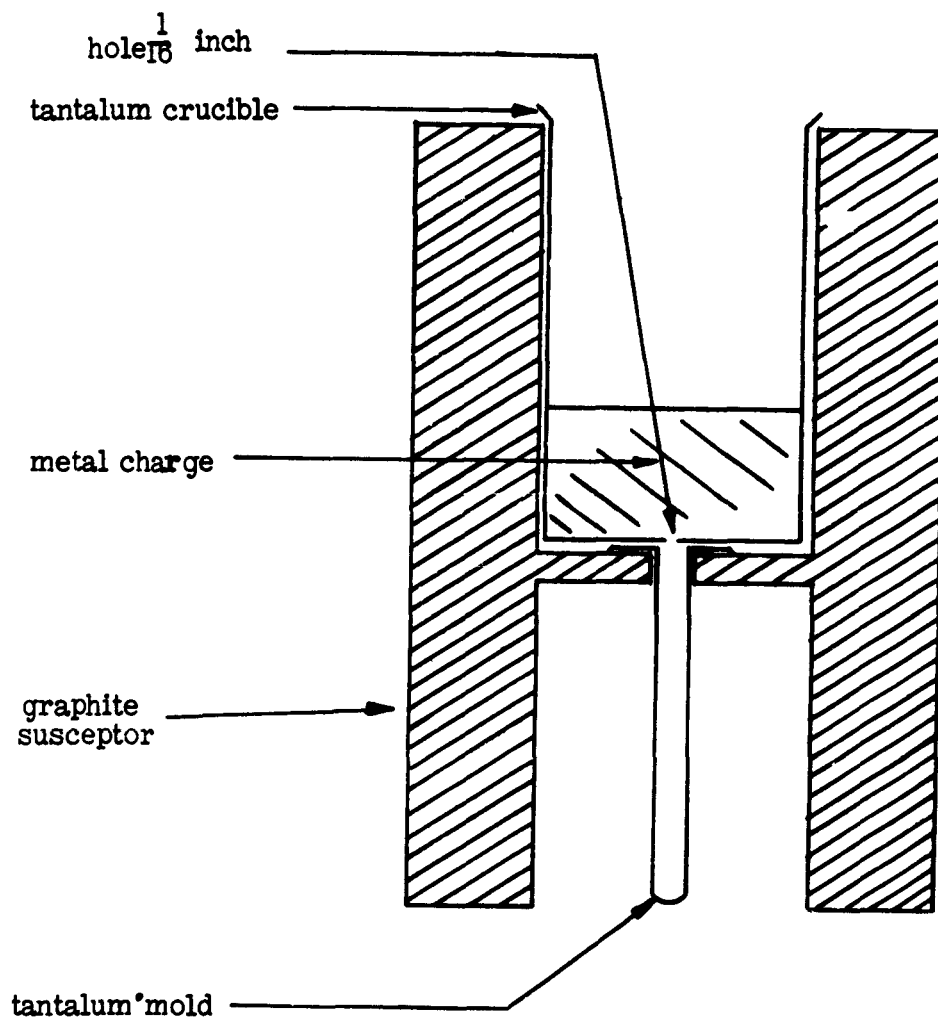
VAPOR PRESSURE DATA

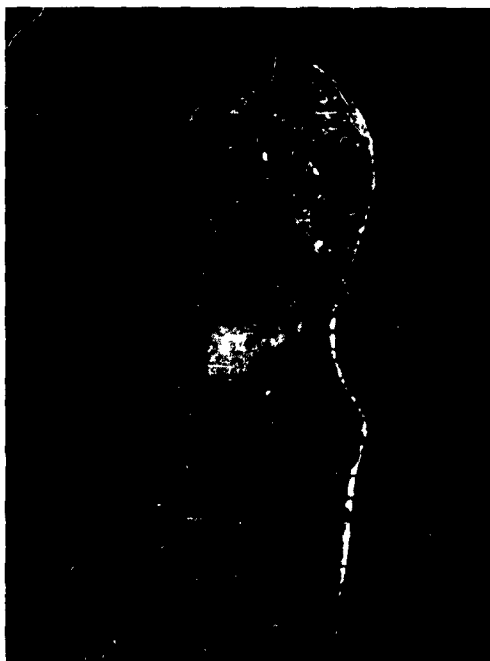
	M.P.	V.P. 2 mm (approx)
Lanthanum	920	2000
Cerium	800	1950
Praseodymium	940	1750
Neodymium	1020	1700
Samarium	1050	860
Europium	890	720
Gadolinium	1310	1700
Terbium	1370	1670
Dysprosium	1380	1520
Holmium	1510	1630
Erbium	1550	1530
Thulium	1600	1220
Ytterbium	800	780
Lutetium	1740	1800

Estimated from graph furnished by Dr. Dahne, I. S. C.

Figure 3

Crucible and mold for casting small charges of High purity metal





Etched Gadolinium Rod
Zone Refined (at breakpoint)
10X Magnification



Single Crystal in
Gadolinium Rod
100X Magnification

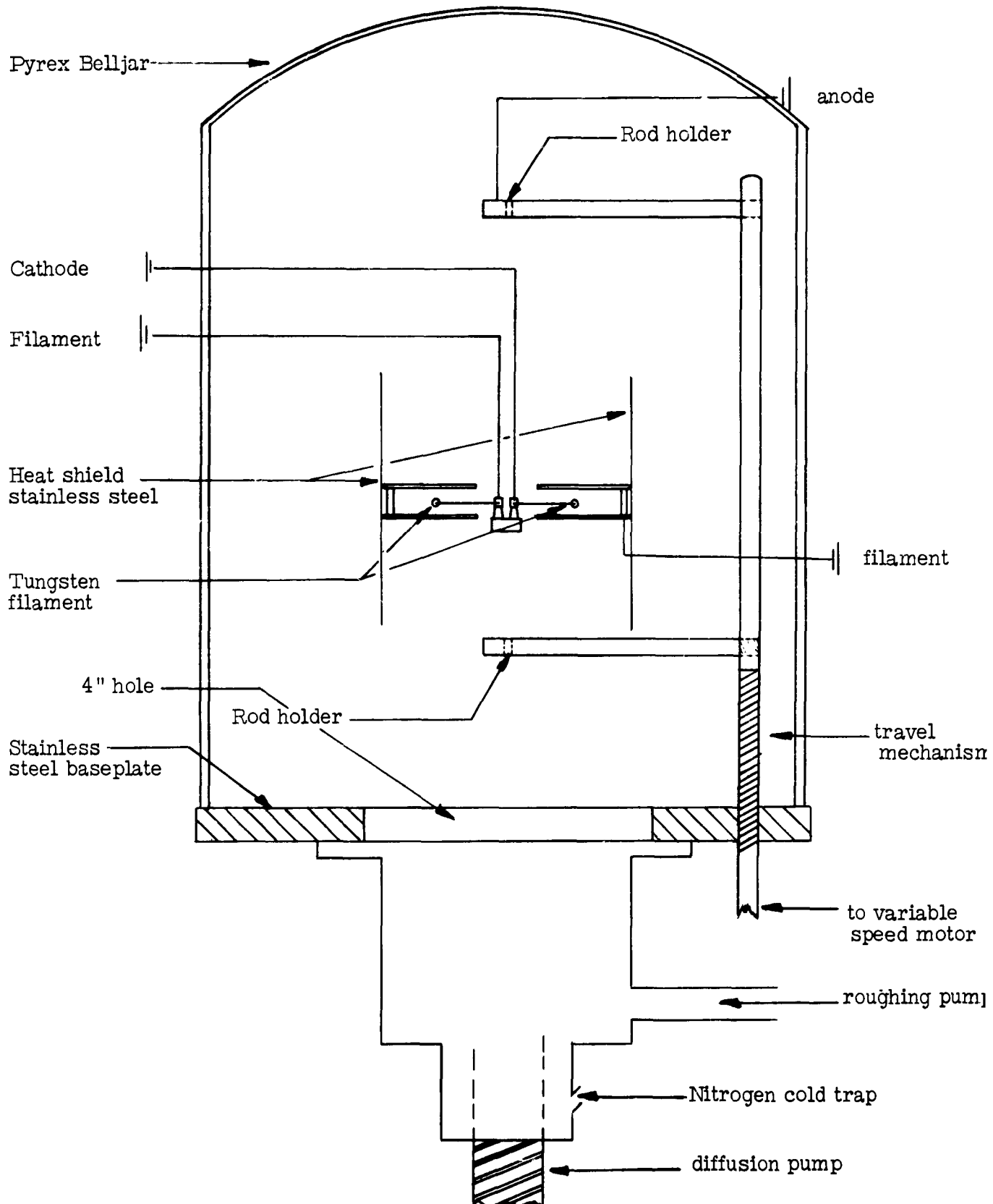


Crystal Formation of a
Gadolinium Rod
10X Magnification



Single Crystal in
Gadolinium Rod
100X Magnification

Electron-beam equipment

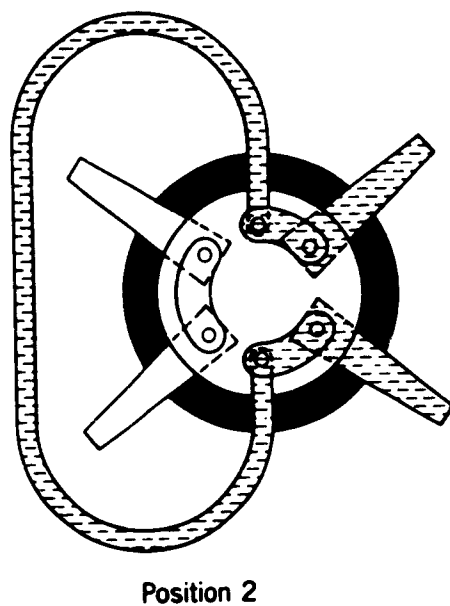
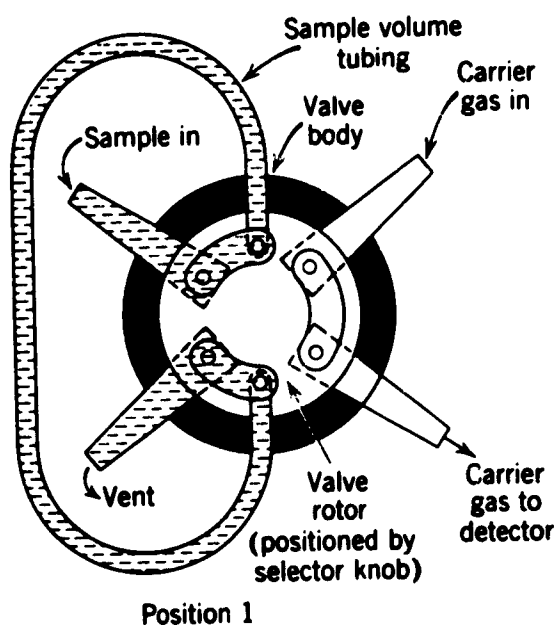
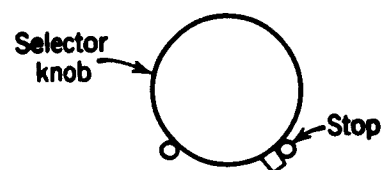
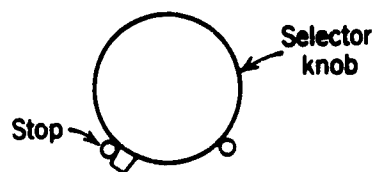


Electron-Beam close-up during outgassing of Gadolinium



Electron-Beam close-up during Zone-refining of Gadolinium





OXYGEN-APPARATUS

